

Interaction of Oppositely Charged Polymer–Surfactant System Based on Surface Tension Measurements

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Abstract

The interaction between oppositely charged polymer-surfactant systems has been studied using surface tension measurements wherein the dependence of interaction phenomenon over the presence of anionic polyelectrolyte sodium carboxymethylcellulose (NaCMC) with variation of tail length of cationic surfactants, cetyltrimethylammonium bromide (CTAB), tetradecyltrimethylammonium bromide (TTAB), and dodecyltrimethylammonium bromide (DTAB) was investigated. It is observed that the cationic surfactants induced cooperative binding with the anionic polyelectrolyte at critical aggregation concentration (cac) and the cac values are considerably lower than the corresponding critical micelle concentration (cmc) for each of the surfactant irrespective of their hydrophobic tail size. The cmc of surfactants were observed at slightly higher surfactant concentration in polyelectrolyte solution than that in pure water. It was found that the surfactants with longer tail size strongly favour the interaction with NaCMC, indicating the dependence of aggregation phenomenon on the tail size of the surfactants.

Keywords

Cationic Surfactants, Anionic Polyelectrolyte, Surface Tension, Tail Size

Introduction

The use of mixtures containing surfactant and polymer has been increased many folds in recent years due to their importance in a variety of industrial applications in cosmetics, personal-care products, foods, pharmaceuticals, detergents, and mineral processing [1,2]. In general, polymers are added to the systems to control rheology, stability of the system, or to manipulate surface adsorption. Interactions within the

mixture are driven by hydrophobic, dipolar, and electrostatic forces. When surfactants are introduced into a solution containing oppositely charged polymer, strong electrostatic interactions are referred as 'strongly interacting system', as the attractive electrostatic forces are extremely important in the oppositely charged polymer and surfactant [3-5]. There has been significant research work focusing on the interaction of oppositely charged polyelectrolytes and surfactants in recent years [6-24].

Surfactants in the presence of an oppositely charged polyelectrolyte start forming aggregates with the polyelectrolyte when surfactant concentration exceeds its critical aggregation concentration (cac). The aggregation of polyelectrolyte and surfactant with opposite charges greatly depends on the properties of surfactant and polyelectrolyte [21]. Polyelectrolyte-surfactant complex formation originates from electrostatic bonding, and is further stabilized by the hydrophobic interactions of surfactant tails [22]. In this process, the counter ion of the polyelectrolyte is replaced by the surfactant ion, and the binding site of the polyelectrolyte and the surfactant forms a neutral ion pair. The large electrostatic attraction in this association process makes binding extremely favourable, and is dependent on the ionic charge density of the polyelectrolyte. Binding in such systems, therefore, occurs at very low free-surfactant concentration [25]. The conformational properties and the dynamic behaviour of the polyelectrolyte chains are determined by the degree of ionization, and the counter ion concentration and distribution [26]. In aqueous solution the solvation properties and the

hydrophobic interactions are also important that strongly influence the conformational properties of the polymer. The counter ions may be solvated in different ways and hence influence the polymer solvation. Low molecular-weight amphiphiles may either redistribute to the polymer segment region or adsorb the backbone affecting the chemical properties of the polymer [27]. Due to the presence of strong electrostatic interaction in oppositely charged systems [28], the polyelectrolyte gives rise to an uneven distribution of ions in solution and the concentration of counterions is strongly enhanced near the polyelectrolyte which decreases rapidly with distance. The uneven distribution of counterions also applies to monomeric surfactant counterions present in the polyelectrolyte solution. The major reason for cooperative binding of surfactant molecules to an oppositely charged polyelectrolyte is the electrostatic stabilization of the surfactant micelles.

Thalberg and Lindman [29] studied the phase behaviour of systems of polyacrylate and cationic surfactants. The association between homopolymer and surfactant reveals that, at low surfactant concentrations, there is no significant association in any polymer concentration. Above cac, the polymer-bound surfactants increase up to certain surfactant concentration which develops linearly with polymer concentration. Micelle formation of surfactant starts as the surfactant concentration increases further after saturation of polymer chains; at this stage free surfactant micelles and surfactant aggregated polymer coexist in the solution. In the presence of polyelectrolyte, micelle size of surfactants is slightly lower than those of micelles formed in the absence of a polymer in solution. In addition to forming micelles, the surfactant can isolate its hydrophobic groups from the aqueous phase by associating them with the hydrophobic part of the polymer.

Experimental Section

Materials

Cetyltrimethylammonium bromide (CTAB, purity>99.0%) from Merck, Germany, tetradecyltrimethylammonium bromide (TTAB, purity=99.0%) from Sigma Aldrich, USA, dodecyltrimethylammonium bromide (DTAB, purity=99.0%) from TCI Tokyo Kasei Kogyo Co. Ltd., Japan, and sodium carboxymethylcellulose (NaCMC, purity>99.0%, molecular weight=90000, degree of substitution=0.7) from Sigma Aldrich, USA, were used

as received for preparation of solutions. Demineralised double-distilled water (specific conductivity~ $1-10 \times 10^{-6}$ S.cm⁻¹) was used in preparation of solutions throughout the experimentation and sufficient time was given for stabilization.

Method

The surface tension measurements were carried out on a Tensiometer (S. D. Hardson, Kolkata, India), by ring detachment technique in which a ring was submerged into the solution under investigation and then force slowly increased to take up the ring on liquid surface and further to detach the ring from surface film of the solution. The surface tension values (γ) were accurate within ± 0.05 mN.m⁻¹. Measurements were performed by progressively adding concentrated stock solution of the individual surfactants in the solution. Surface tension data were taken at a time interval of five minutes after stirring the solutions at 30 ± 1 °C temperature.

Results and Discussion

The tensiometric plot of CTAB shows a sharp decrease in surface tension with a slight increase in [CTAB] up to cac, then it approximately keeps constant giving 'first plateau' until critical saturation concentration C_s . A further decrease in surface tension is observed up to cmc, beyond which it further stabilizes, giving 'second plateau' due to formation of free micelles in the solution [30]. The plot of CTAB in pure water (Figure 1a) shows only one critical concentration (i.e., at cmc), while in the presence of NaCMC three critical concentrations (first at cac, second at C_s and third at cmc) are observed. This indicates the influence of NaCMC in the solution and its association with the cationic surfactant CTAB. C_s represents the critical saturation concentration of the surfactant (Figure 1b) when all the binding sites on polyelectrolyte are saturated due to adsorption of CTAB over polymer backbone. During this association process (at first plateau), surface tension of the solution is almost constant as the added surfactant get associated with the polyelectrolyte molecules in the solution and surfactant free molecules are not available to affect the surface properties of the solution. Cationic head groups of surfactant individually bind to the anionic carboxylate groups on the polymer chains due to electrostatic attraction. When all the binding sites on polyelectrolyte molecules are saturated with surfactant molecules, surface tension starts decreasing with increase in CTAB concentration further till a certain

concentration, termed as critical micelle concentration (cmc) is reached. At cmc, the micellization of polymer bound surfactant occurs resulting in the formation of insoluble polymer-surfactant complexes. This suggests that the polymer-surfactant system also undergoes a two-stage interaction process where the surfactant binds to the polyelectrolyte due to electrostatic attraction; thereafter, the micellization of polymer-bound surfactant molecules occurs as reported in literature [31-33].

Almost similar trends of surface tension plots were obtained with other surfactants having the same head group but a changed hydrophobic tail (i.e., TTAB and DTAB) (Figures 2 and 3). A significant change in the cmc of the cationic surfactants CTAB, TTAB, and DTAB was observed as represented in Figure 4, which indicates that the cmc found in the presence of NaCMC is higher in comparison to that of the pure water. This is due to the association phenomenon and formation of polymer-surfactant complexes as a result of polymer surfactant interaction. The surface tension values at cmc (γ_{cmc}) plotted in Figure 5 show a less significant variation in the presence of polyelectrolyte, which is in agreement with the literature [3, 31]. Figure 6 shows the schematic illustration of the complex formation after cmc in an oppositely charged polymer-surfactant system in aqueous medium.

Conclusions

The interaction between anionic polyelectrolyte sodium carboxymethylcellulose in aqueous solution with cationic surfactants cetyltrimethylammonium bromide, tetradecyltrimethylammonium bromide, and dodecyltrimethylammonium bromide has been studied using surface tension measurements. It is evident from the results that the cationic surfactants interact strongly with the oppositely charged anionic polymer. The analysis of cac and cmc of cationic surfactants indicates clearly the existence of strong electrostatic interactions of these surfactants with oppositely charged NaCMC. At cac, the surfactant binds to the polymer due to strong electrostatic interactions, and after saturation of the binding sites of the polyelectrolyte at critical saturation concentration, the surface tension decreases further on increasing surfactant concentration until it reaches the cmc of the surfactant. The study of tail size variation on interaction indicates that the surfactants with longer tail size favour the interaction.

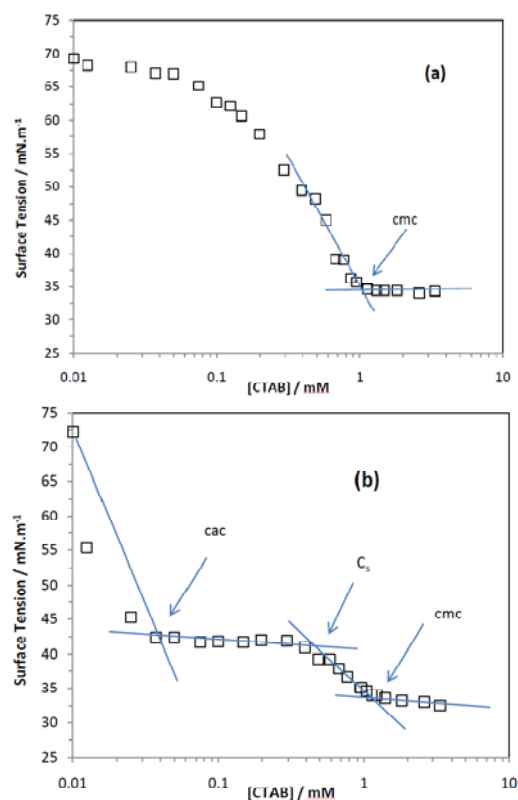


FIG. 1 VARIATION OF SURFACE TENSION (γ) WITH CTAB CONCENTRATION IN PURE WATER (A), AND 0.01 G% NaCMC AQUEOUS MEDIUM (B) AT 30 °C

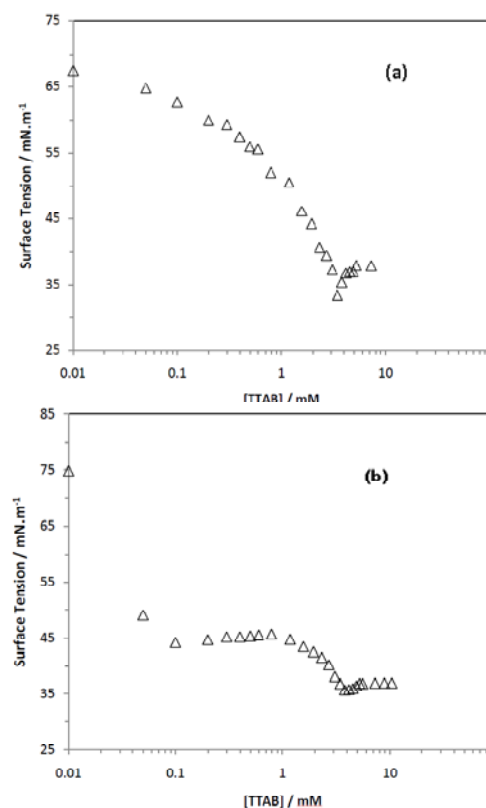


FIG. 2 VARIATION OF SURFACE TENSION (γ) WITH TTAB CONCENTRATION IN PURE WATER (A), AND 0.01 G% NaCMC AQUEOUS MEDIUM (B) AT 30 °C

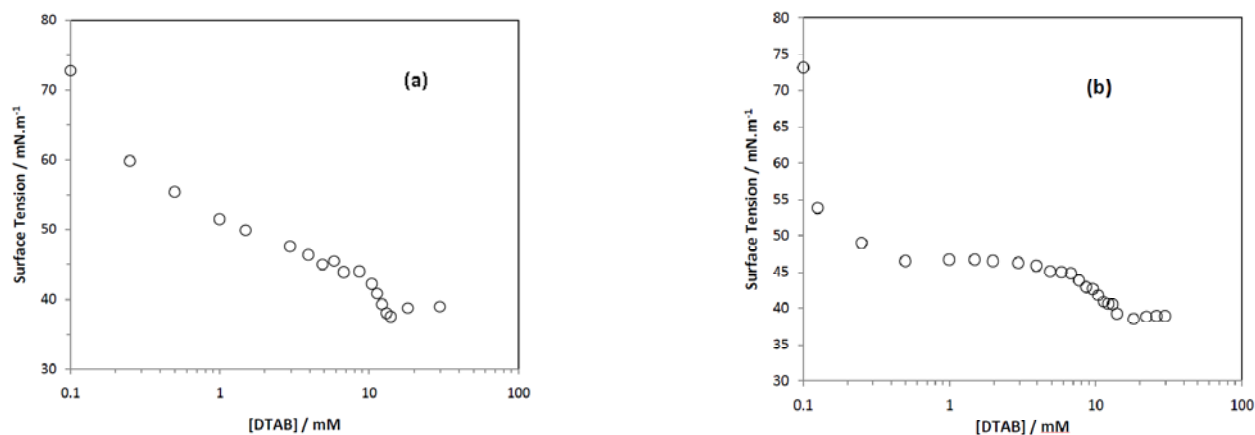


FIG. 3 VARIATION OF SURFACE TENSION (γ) WITH DTAB CONCENTRATION IN PURE WATER (A), AND 0.01 G% NACMC AQUEOUS MEDIUM (B) AT 30 °C

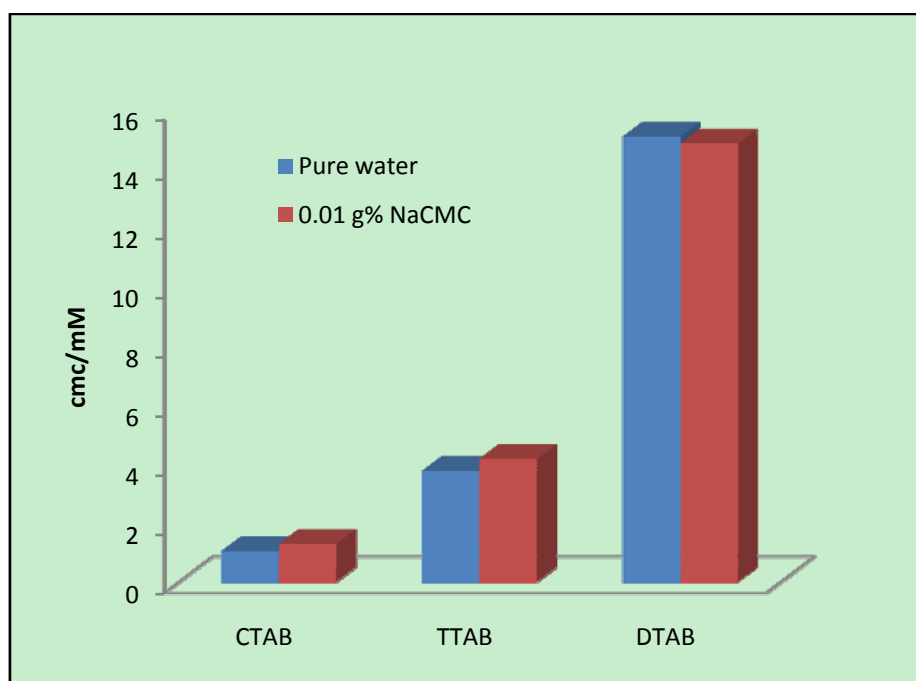


FIG. 4 COMPARISON OF CRITICAL MICELLE CONCENTRATION (CMC) OF CTAB, TTAB, AND DTAB IN PURE WATER AND IN POLYELECTROLYTE SOLUTION AT 30 °C (BASED ON SURFACE TENSION MEASUREMENTS)

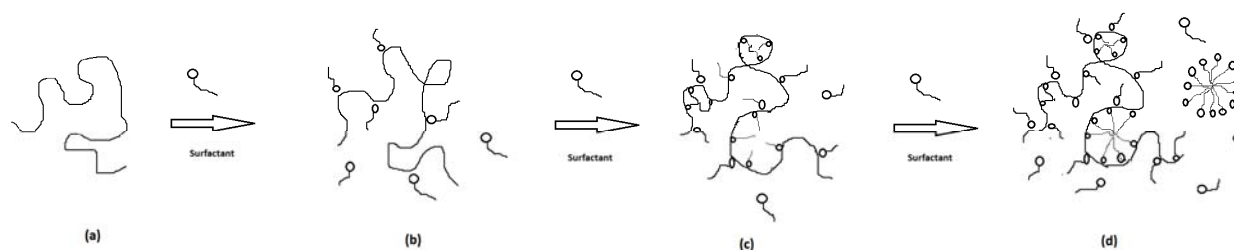


FIG. 6 SCHEMATIC ILLUSTRATION OF POLYELECTROLYTE CHAIN (A), POLYMER SURFACTANT ASSOCIATION (B), BOUND-SURFACTANT MOLECULES AFTER CAC (C), AND COMPLEX FORMATION AFTER CMC (D) IN AN OPPOSITELY CHARGED POLYMER-SURFACTANT SYSTEM IN AQUEOUS MEDIUM

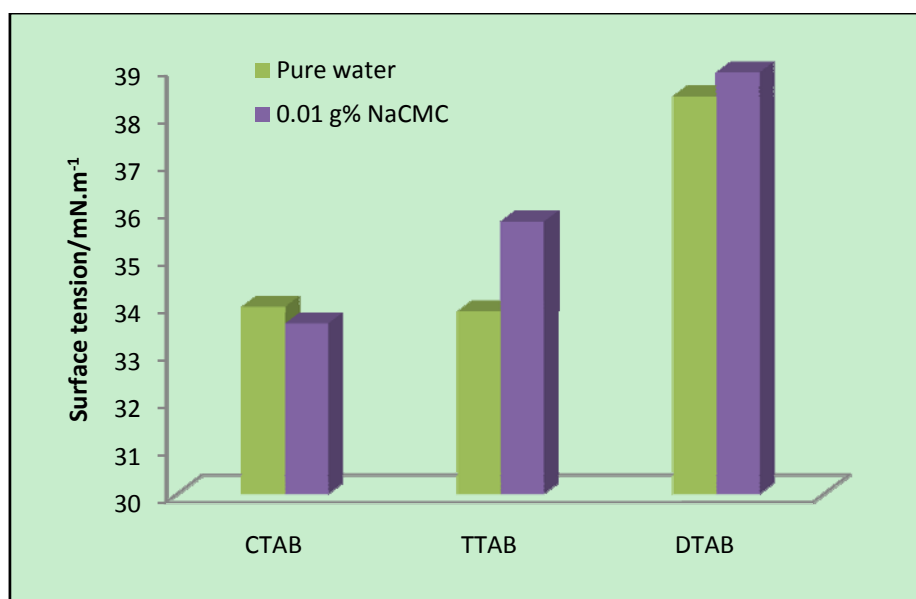


FIG. 5 COMPARISON OF SURFACE TENSION AT CMC (γ_{CMC}) OF CTAB, TTAB, AND DTAB IN PURE WATER AND IN POLYELECTROLYTE SOLUTION AT 30 °C (BASED ON SURFACE TENSION MEASUREMENTS)

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